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Reactivity of a C,N-Chelated Stannoxane[†]

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*Summary: The stannylene $\{2\text{-}[(CH_3)_2NCH_2]_2C_6H_4\}_2Sn$ (**1**) did not react with CO_2 at room temperature and atmospheric pressure, but its oxidation product $\{\{2\text{-}[(CH_3)_2NCH_2]_2C_6H_4\}_2Sn(\mu\text{-}O)\}_2$ (**2**) is very reactive toward CO_2 to give the cyclic compound $\{\{2\text{-}[(CH_3)_2NCH_2]_2C_6H_4\}_2Sn\}_2(\mu\text{-}O)(\mu\text{-}CO_3)$ (**2b**). The product of reaction of **2** with silicon grease is also a cyclic compound with an eight-membered ring, $\{\{\{2\text{-}[(CH_3)_2NCH_2]_2C_6H_4\}_2Sn\}(Me_2SiO)\}_2$ (**2c**), as the structural characterization revealed (XRD). Triphenylsilanol condensates with **2** to form $\{2\text{-}[(CH_3)_2NCH_2]_2C_6H_4\}_2Sn(OSiPh_3)_2$ (**2b**). The reaction of **2** with ethylene glycol gave the cyclic compound $\{2\text{-}[(CH_3)_2NCH_2]_2C_6H_4\}_2Sn(OCH_2CH_2O)\cdot{}^1/_2(HOCH_2CH_2OH)$ (**2e**).*

The reactivity of higher congeners of carbenes, e.g. silylenes, germylenes, stannylenes, and plumbylenes, has been studied very extensively over the last 20 years.[1]

The stannylene $(L^{CN})_2Sn$[2] (**1**), where L^{CN} is the chelating ligand 2-((dimethylamino)methyl)phenyl, can be oxidized with excess oxygen, nitrous oxide, or the TEMPO free radical to give the dimeric stannoxane $[(L^{CN})_2Sn]_2(\mu\text{-}O)_2$ (**2**), which is in dynamic equilibrium with its monomeric form in benzene solution. In the solid state, the tetraoxatetrastannacycle *cyclo*-$[(L^{CN})_2SnO]_4$ can be crystallized from diethyl ether and the trioxatristannacyclic complex of formula *cyclo*-$[(L^{CN})_2SnO]_3$ from hexane solution.[3] In this paper, we expand the reactivity studies of **2** toward other reagents.

Results and Discussion

When the oxidation product of **1**, $[(L^{CN})_2Sn]_2(\mu\text{-}O)_2$ (**2**) (obtained either with oxygen or N_2O), was left in air, compound **2b** ($\{\{2\text{-}[(CH_3)_2NCH_2]_2C_6H_4\}_2Sn\}_2(\mu\text{-}O)(\mu\text{-}CO_3)$) was isolated as the sole product after a few minutes (Figure 1). This behavior is similar to the well-known reaction of $Bu_3Sn{-}O{-}SnBu_3$ with CO_2, which affords the bridged carbonato species $Bu_3Sn\text{-}OCO_2{-}SnBu_3$[4] and was also observed in the case of C,N-chelated triorganotin(IV) oxides and hydroxides.[5]

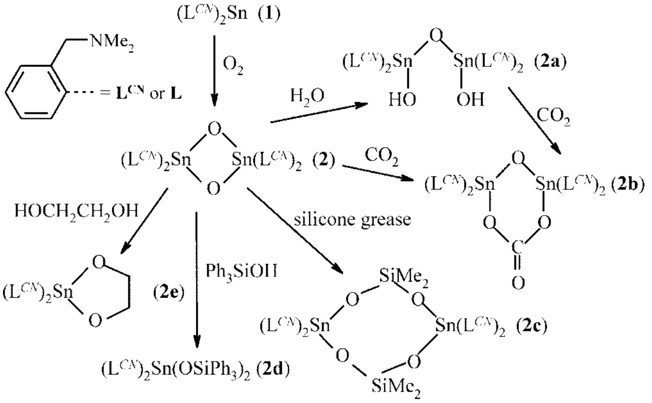

Figure 1. Reactivity of **1**.

Similar compounds ($(R_2Sn)_2OCO_2$) with 5-fold-coordinated tin atoms were suggested to be products of the reaction of dialkyltin dihalides with alkali-metal carbonates in water.[6]

Compound **2b** is a cyclic oxo–carbonato-bridged dinuclear species containing a six-membered, rather puckered ring (Figure 2). The O2 and O3 atoms lie above and below the plane defined by Sn1, O1, Sn2, C=O(4), and all the nitrogen atoms coordinated to the tin atoms. It seems that one of the tin atoms (Sn1) is six-coordinated in a distorted-octahedron-like geometry with nitrogen donor (N1 and N2) and oxygen bridging atoms in mutual cis positions and carbon atoms of the ligands in a trans arrangement. The second tin atom has only one nitrogen atom (N4) coordinated with an Sn–N distance comparable to that of diorganotin dihalides with the same ligand.[7] The second nitrogen atom is on the border of possible interaction. The carbonate fragment is bonded to both tin atoms by oxygen atoms O2 and O3 with bond lengths comparable to those of the tin–O1 bridge and to those in literature data. On the other hand, O4 has no interaction to the adjacent

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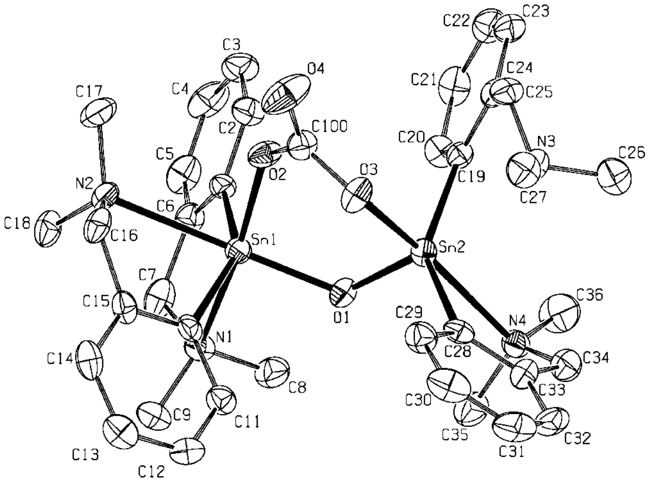

Figure 2. ORTEP presentation at the 50% probability level of the molecular structure of **2b**. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Sn(1)−O(1) = 1.988(3), Sn(1)−O(2) = 2.079(4), Sn(2)−O(1) = 1.966(4), Sn(2)−O(3) = 2.080(4), Sn(1)−N(1) = 2.653(5), Sn(1)−N(2) = 2.614(4), Sn(2)−N(3) = 2.874(5), Sn(2)−N(4) = 2.544(4), C(100)−O(2) = 1.312(2), C(100)−O(3) = 1.322(2), C(100)−O(4) = 1.215(8); O(3)−Sn(2)−N(4) = 164.23(14), Sn(2)−O(1)−Sn(1) = 121.29(19), O(4)−C(100)−O(2) = 121.4(5).

acceptor atoms, and from C100−O4 bond shortening in comparison with O2 and O3, the double-bond character is clearly seen.

In the ^{119}Sn NMR spectra of **2b** at various temperatures, there is only a slight dependence of chemical shift observed (−309.2 ppm at 350 K and −315.8 ppm at 220 K) typical for six-coordinate species. On the other hand, in the ^{1}H NMR spectra two sets of signals appear for each nonequivalent NCH$_2$ group as two AX patterns. All signals coalesce as the temperature is increased to very broad signals at 350 K. For the carbonate group in the ^{13}C NMR spectrum, over the whole temperature range there is only one sharp signal at 161.9 ppm with tin satellites visible, which corresponds to recently published bridging carbonates with no interaction of the C=O group.[5] Also in the IR spectrum, the wavelength 1587 cm^{-1} similar to previous findings supports the suggestion that the structure of **2b** is the same in the solid and in solution.

In view of this reactivity of complex **2** with carbon dioxide, the stannoxane **2** was tested as a catalyst for the formation of cyclic carbonates and aliphatic polycarbonates by reaction of epoxides with CO$_2$. Propylene oxide and cyclohexene oxide were used in preliminary screening tests. Only the test involving propylene oxide and complex **2** showed the formation of propylene carbonate in measurable amounts (yield estimated to be under 5% molar), without formation of the related aliphatic polycarbonate. The reaction with cyclohexene oxide did not lead to the formation of organic carbonates. Other catalytic tests carried out with ethanol, carbon dioxide, and triethyl orthoacetate (as water-trapping agent) in order to produce a carbonic acid hemiester (LSn−CO$_2$−OEt) or, better, diethyl carbonate were also unsuccessful.

A hypothetical mechanism for the formation of propylene carbonate in the presence of compound **2** is proposed in Figure S2 (Supporting Information).

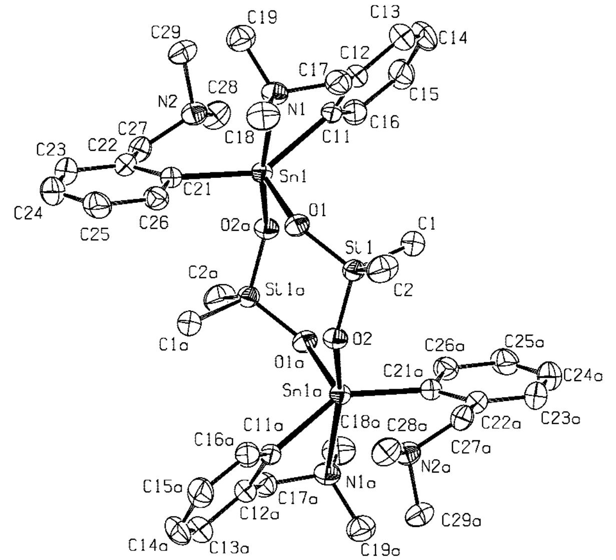

Figure 3. ORTEP presentation at the 50% probability level of the molecular structure of **2c**. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Sn(1)−O(1) = 1.9951(19), Sn(1)−O(2) = 1.9962(19), Sn(1)−C(21) = 2.126(3), Sn(1)−C(11) = 2.131(3), Si(1)−O(2) = 1.613(2), Si(1)−O(1) = 1.620(2), Sn(1)−N(1) = 2.717(2), Sn(1)−N(2) = 2.736(3); O(1)−Sn(1)−O(2) = 98.98(8), O(2)−Si(1)−O(1) = 112.53(11), Si(1)−O(1)−Sn(1) = 134.11(12), Si(1)−O(2)−Sn(1) = 137.31(12).

An unusual product of the accidental "transesterification" of silicone grease ({{{2-[(CH$_3$)$_2$NCH$_2$]$_2$C$_6$H$_4$}$_2$Sn}(Me$_2$SiO)}$_2$ (**2c**)) (Figure 3) could be also isolated as a minor product when **2a** was refluxed in toluene under an argon atmosphere in order to remove water and prepare **2**. **2c** can be compared to various related fortuitous results[8] where silicone grease is incorporated into the structure, but only the tricyclic ring system reported by Pannell and co-workers is a tin-containing species.[9] However in our case, **2c** is more likely the product of a "transesterification" of (Me$_2$SiO)$_n$ with [(L^{CN})$_2$Sn]$_2$(μ-O)$_2$ than a product of hydrolysis and self-assembly as in Pannell's case (t-Bu$_4$Sn(Me$_2$Si)O$_3$·t-Bu$_2$Sn(OH)$_2$).[9] The same C,C-transoid geometry is concluded from two broad signals for NCH$_2$ groups found in the ^{1}H NMR spectrum of **2c**. The tin atoms in **2c** are again six-coordinated, as seen from the ^{119}Sn NMR spectrum and chemical shift value (− 359.9 ppm) compared to similar compounds.

Similar systems[10] revealed two main structural motifs, chair- and boatlike, where *n*-butylferrocenylsilyl-[10a] and diphenylsilyl-substituted[10b] systems are boatlike, *tert*-butylsilyl species[10c] oscillate between both extremes, and isopropylsilyl-substituted[10e] systems were found to be almost planar. The structure of **2c** can be related to the structure of compounds where two 3-(dimethylamino)propyl groups are chelating ligands and the silicon atom is substituted by two phenyl groups.[10d] **2c** has a chairlike structure with both tin atoms in a distorted -octahedral geometry, where the C,C-transoidal arrangement is applied. The C1−Sn−C11 angle is 143.85(11)°, in comparison to the compound described in ref 10d to be 154.5(2)°. Two intramolecular connections, Sn(1)−N(1) = 2.717(2) Å and Sn(1)−N(2) = 2.736(3) Å, which complete the octahedral coordination geometry, are medium strong and comparable to those in **2b** and previously reported bis-chelated dihalides.[7]

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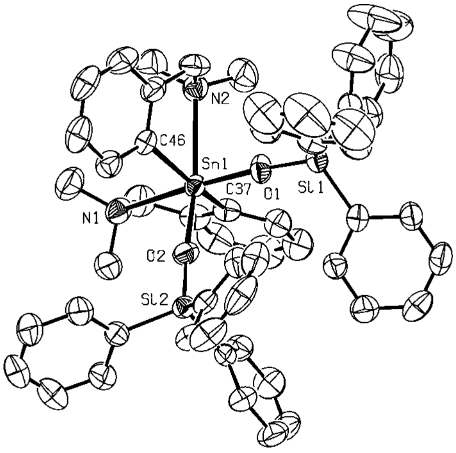

Figure 4. ORTEP presentation at the 50% probability level of the molecular structure of **2d**. Hydrogen atoms and one of the independent molecules are omitted for clarity. Selected interatomic distances (Å) and angles (deg), with appropriate parameters for the geometrically independent molecule given in parentheses: Sn(1)−O(1) = 2.008(3) (2.005(4)), Sn(1)−O(2) = 1.997(3) (1.987(4)), Sn(1)−N(1) = 2.605(4) (2.663(5)), Sn(1)−N(2) = 2.715(4) (2.675(15)), Si(1)−O(1) = 1.590(3) (1.590(4)), Si(2)−O(2) = 1.592(3) (1.594(4)); O(1)−Sn(1)−O(2) = 95.19(14) (96.38(16)), Si(1)−O(1)−Sn(1) = 172.9(2) (172.1(2)), Si(2)−O(2)−Sn(1) = 175.0(2) (177.5(3)), N(1)−Sn(1)−O(1) = 170.58(13) (168.46(14)), N(2)−Sn(1)−O(2) = 169.67(13) (171.9(3)).

To evaluate this reactivity, the reaction of oxide **2** and 2 equiv of triphenylsilanol was carried out. The hexane solution of the reaction mixture became opalescent immediately, yielding **2d** essentially quantitatively. **2d** is unstable in air and in moist chloroform solution is converted to carbonate **2b** and oxide dihydroxide **2a**. The ^{119}Sn NMR shift value (−355.4 ppm) for **2d** in benzene solution is close to the shift found for **2c** and is attributed to the six-coordinate tin atom in solution. The ^{1}H as well as ^{119}Sn NMR spectra reveal patterns similar to those found for **2c**, where these are due to the C,C-transoid geometry and mutual cis positions for nitrogen donors (Figure 4) similarly as found for **2b**,**c** and for bis-chelated tin dihalides.[7]

The reaction of $[(L^{CN})_2Sn]_2(\mu\text{-}O)_2$ with an excess of ethylene glycol also was examined. In refluxing toluene solution using a Dean−Stark apparatus, the reaction gave after crystallization a complex product of composition $\{2\text{-}[(CH_3)_2NCH_2]_2C_6H_4\}_2\text{-}Sn(OCH_2CH_2O)\cdot{}^1/_2HOCH_2CH_2OH$ (**2e**$\cdot{}^1/_2HOCH_2CH_2OH$ (Figure 5 and Figure S2 (Supporting Information)), whose excess ethylene glycol could be removed by vacuum distillation to give $\{2\text{-}[(CH_3)_2NCH_2]_2C_6H_4\}_2Sn(OCH_2CH_2O)$ (**2e**).

The structure of **2e**$\cdot{}^1/_2HOCH_2CH_2OH$ is comparable to the structures of **2b**−**d**, where the intramolecular Sn−N contacts in this complex are a bit stronger, probably due to strain in the five-membered ring. Each of the two molecules of **2e** are interconnected through one molecule of ethylene glycol via H bridges (Figure S2 (Supporting Information); the OH···O distance is 2.661(3) Å). On the basis of the NMR parameters and the spectral patterns, also the structure of **2e** in solution seems to be very close to those of the aforementioned structures **2b**−**d**.

The activation of the aforementioned molecules was studied by a theoretical approach as well (see the Supporting Information). Thermodynamic parameters of reactions of **2** with CO_2, silicon grease, and ethylene glycol were calculated theoretically (Scheme S1, Supporting Information). Addition of one molecule of CO_2 to **2**, yielding **2b**, is exothermic ($\Delta H° = -12.2$ kcal/mol), but the Gibbs free energy is slightly positive ($\Delta G° = 0.4$ kcal/mol). Thus, the CO_2 unit in **2b** is quite labile. This could be the reason for the high catalytic activity of **2b** in the formation of carbonates.

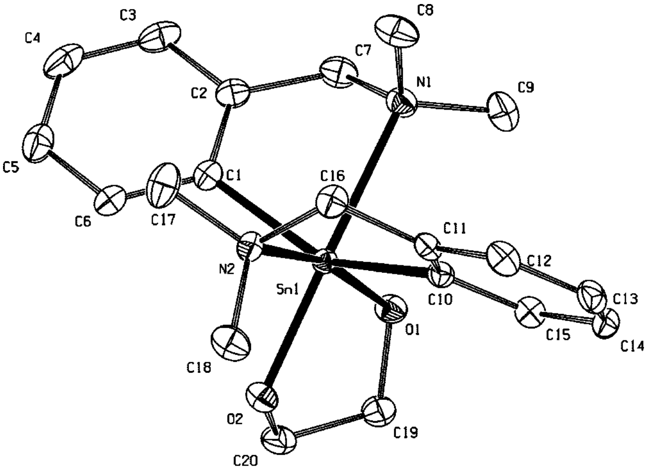

Figure 5. ORTEP presentation at the 50% probability level of the molecular structure of **2e**$\cdot{}^1/_2HOCH_2CH_2OH$. Hydrogen atoms and the ethylene glycol molecule are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Sn(1)−O(1) = 2.0360(19), Sn(1)−O(2) = 2.058(2), Sn(1)−N(1) = 2.519(2), Sn(1)−N(1) = 2.640(2); O(1)−Sn(1)−O(2) = 83.36(8), O(2)−Sn(1)−N(1) = 163.01(8).

Experimental Section

General Methods. NMR Spectroscopy. The NMR spectra were recorded as solutions in toluene-d_8 or benzene-d_6 on a Bruker Avance 500 spectrometer (equipped with Z-gradient 5 mm probe) at 220−300 K for ^{1}H (500.13 MHz) and ^{119}Sn{^{1}H} (186.50 MHz). The solutions were obtained by dissolving 40 mg of each compound in 0.5 mL of deuterated solvent. ^{13}C{^{1}H} NMR spectra were measured at 90.35 MHz in a 5 mm wide-zone tunable sampler. The values of ^{1}H chemical shifts were calibrated to the internal standard tetramethylsilane ($\delta(^1H)$ 0.00 ppm) or to residual signals of benzene ($\delta(^1H)$ 7.16 ppm), toluene ($\delta(^1H)$ 2.09 ppm). The values of ^{13}C chemical shifts were calibrated to signals of benzene ($\delta(^{13}C)$ 128.3 ppm), and ^{119}Sn chemical shifts to external Me_4Sn (0.0 ppm).

X-ray Crystallography. Data for crystals were collected on a Nonius KappaCCD diffractometer using Mo Kα radiation ($\lambda = 0.710\,73$ Å), and a graphite monochromator. The structures were solved by direct methods (SIR92[11]). All reflections were used in the structure refinement based on F^2 by full-matrix least-squares techniques (SHELXL97[12]). Heavy atoms were refined anisotropically. Hydrogen atoms were mostly localized on a difference Fourier map; however, to ensure uniformity of the treatment of the crystal, all hydrogen atoms were recalculated into idealized positions (riding model) and assigned temperature factors $U_{iso}(H) = 1.2[U_{eq}(\text{pivot atom})]$ or of $1.5U_{eq}$ for the methyl moiety. Absorption corrections were carried out using Gaussian integration from the crystal shape for **2b**,**d**,[13] by SORTAV for **2e**$\cdot{}^1/_2HOCH_2CH_2OH$,[14] or by SADABS[15] for **2c**. The disorder of one of the ligands in one of the two independent molecules in **2d** was solved by splitting appropriate atoms to two positions.

A full list of crystallographic data and parameters, including fractional coordinates, has been deposited at the Cambridge Crystal-

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lographic Data Center, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, int. code +44(1223)336-033; e-mail, deposit@ccdc.cam.ac.uk) with CCDC deposition numbers 684119−684124.

Calculation Procedure. All calculations were done at the DFT level of theory. Geometry optimizations were carried out using the PBE generalized gradient functional.[16,17] The triple-ζ valence basis set including polarization functions TZ2P {3,1,1/3,1,1/1,1} for Sn, C, N, and O atoms and {3,1,1/1} for H atoms was used. The innermost electrons for Sn, C, N, and O atoms were treated using the ECP-SBKJC relativistic effective core potentials.[18] Total energies *E*, zero-point vibration energies ZPE, $E° = E + \mathrm{ZPE}$, $H°$, and $G°$ were calculated for all stationary points. Vibration frequencies were used to characterize stationary points as minima. All calculations were performed using the PRIRODA program.[19] The same approach and program were previously used in studies of various types of germanium and tin compounds.[20]

Synthetic Procedures. $(\mathrm{L}^{CN})_2\mathrm{Sn}$ (1)[2] and $\{\{2\text{-}[(\mathrm{CH_3})_2\mathrm{NCH_2}]_2\mathrm{C_6H_4}\}_2\mathrm{Sn}(\mu\text{-O})\}_2$ (2).[3] These compounds were prepared according to published procedures. All solvents and starting compounds were obtained from commercial sources (Sigma-Aldrich). Stopcocks were greased and additional experiments made using Dow Corning high-vacuum grease. Toluene, THF, diethyl ether, benzene, *n*-hexane, and *n*-pentane were dried over and distilled from sodium, degassed, and stored over potassium mirror under argon. CO_2 was absorbed from air or used dry from a cylinder to give the same results. Standard Schlenk techniques were used for all manipulations under an argon atmosphere.

$\{\{2\text{-}[(\mathrm{CH_3})_2\mathrm{NCH_2}]_2\mathrm{C_6H_4}\}_2\mathrm{Sn}\}_2(\mu\text{-O})(\mu\text{-CO}_3)$ (2b). This compound was prepared by bubbling dried CO_2 into a Et_2O solution (ca. 10% w/w) of **2** (2 g, 2.5 mmol) for 5 min. A white precipitate of **2b** was washed with pentane (10 mL) and crystallized from THF to give 1.77 g of white solid (yield 84%). ^{1}H NMR (500.13 MHz, C_6D_6, 300 K, ppm): 7.95 (d, 2H, H(6), $^3J(^1\mathrm{H},^1\mathrm{H}) = 6.8$ Hz, $^3J(^1\mathrm{H},^{119}\mathrm{Sn}) = 68$ Hz); 7.56 (d, 2H, H(6), $^3J(^1\mathrm{H},^1\mathrm{H}) = 6.6$ Hz, $^3J(^1\mathrm{H},^{119}\mathrm{Sn}) = 72$ Hz); 7.36, 7.27, 7.21 (m, 8H, H(4,5)); 7.09, 6.85 (d and d of d, 4H, H(3)); 3.80, 3.69, 3.49, 3.23 (four equivalent doublets, 8H, NCH_2); 2.01 and 1.92 (broad singlets, 24H, $N(CH_3)_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 300 K, ppm): 161.9 ($^3J(^{13}\mathrm{C},^{119}\mathrm{Sn}) = 21.5$ Hz), 142.9, 142.6, 142.1, 140.8, 137.6, 137.0, 130.2, 129.0, 128.7, 128.2, 127.8, 127.6, 127.2, 126.6, 126.4, 125.3, 124.8, 64.7, 64.4, 46.2. ^{119}Sn{^{1}H} NMR (C_6D_6, 300 K, ppm): − 311.9, ($^3J(^{119}\mathrm{Sn},^{117}\mathrm{Sn}) = 286$ Hz). IR (in KBr): 1587 cm^{-1} as ν_3 of CO_3^{2-}. Anal. Found: C, 52.3; H, 5.6; N, 6.5. Calcd for $C_{37}H_{48}N_4O_4Sn_2$ (850.20): C, 52.27; H, 5.69; N, 6.59. Mp: 226−230 °C with loss of CO_2 (detected by DSC).

$\{\{\{2\text{-}[(\mathrm{CH_3})_2\mathrm{NCH_2}]_2\mathrm{C_6H_4}\}_2\mathrm{Sn}\}(\mathrm{Me_2SiO})\}_2$ (2c). This compound was first observed as a minority product when **2a** was refluxed in toluene in a Dean−Stark apparatus, in order to prepare **2**, as a product of reaction with silicone grease used for greasing of apparatus joints. **2c** can be prepared by two alternative pathways. (i) $2\text{-}[(\mathrm{CH_3})_2\mathrm{NCH_2}]_2\mathrm{C_6H_4}\}_2\mathrm{SnBr_2}$ (1 g, 1.83 mmol), Me_2SiCl_2 (0.236 g, 1.83 mmol), and 4 equiv of NaOH (0.3 g) were stirred overnight in 20 mL of benzene and 20 mL of water. After separation of layers, the organic phase was dried with sodium sulfate and evaporated in vacuo. The crude product was extracted with dichloromethane to give a mixture of $2\text{-}[(\mathrm{CH_3})_2\mathrm{NCH_2}]_2\mathrm{C_6H_4}\}_2\mathrm{SnBr_2}$ and **2c**. (ii) **2** (1 g, 1.25 mmol) was refluxed with hexamethyltrisiloxane (0.3 g, 1.25 mmol) or octamethylcyclotrisiloxane (0.37 g, 1.25 mmol) in xylene for 12 h. The solvent was removed by vacuum and the crude product washed twice with warm hexane (30 mL). The solid was extracted with dichloromethane to give after crystallization 0.15 g of **2c** as a white solid (yield 13%). ^{1}H NMR (500.13 MHz, C_6D_6, 300 K, ppm): 8.28 (broad, 4H, H(6)); 7.34 (m, 8H, H(4,5)); 6.85 (d, 4H, H(3), $^3J(^1\mathrm{H},^1\mathrm{H}) = 7.0$ Hz); 3.53 and 2.96 (two broad signals, 8H, NCH_2); 1.81 (broad, 24H, $N(CH_3)_2$); 0.07 (s, 8H, $SiMe_2$). ^{119}Sn{^{1}H} NMR (C_6D_6, 300 K, ppm): −359.9. Anal. Found: C, 50.2; H, 6.2; N, 5.8. Calcd for $C_{40}H_{60}N_4O_4Si_2Sn_2$ (954.50): C, 50.33; H, 6.34; N, 5.87. Mp: 222−225 °C.

$\{2\text{-}[(\mathrm{CH_3})_2\mathrm{NCH_2}]_2\mathrm{C_6H_4}\}_2\mathrm{Sn}(\mathrm{OSiPh_3})_2$ (2d). This compound was prepared by mixing **2** (1 g, 1.25 mmol) and 2 equiv of Ph_3SiOH (2.04 g, 7.4 mmol) in benzene (20 mL). Immediate formation of opalescence was observed and the solvent removed in vacuo. The remaining white solid was crystallized from diethyl ether, giving 2.18 g of **2d** (93% yield). ^{1}H NMR (500.13 MHz, C_6D_6, 300 K, ppm): 8.45 (d, 2H, H(6), $^3J(^1\mathrm{H},^1\mathrm{H}) = 6.8$ Hz, $^3J(^1\mathrm{H},^{119}\mathrm{Sn}) = 78$ Hz); 7.79 (d, 12H, H (ortho-SiPh), $^3J(^1\mathrm{H},^1\mathrm{H}) = 6.6$ Hz); 7.34 (m, 4H, H(4,5)); 7.31 (m, 18H, H (meta and para SiPh)); 7.01 (m, 2H, H(3)); 3.57 and 2.78 (AX spin system, 4H, NCH_2); 1.48 (s, 12H, $N(CH_3)_2$). ^{119}Sn{^{1}H} NMR (C_6D_6, 300 K, ppm): − 355.6. Anal. Found: C, 69.3; H, 6.0; N, 3.1. Calcd for $C_{54}H_{54}N_2O_2Si_2Sn$ (937.91): C, 69.15; H, 5.8; N, 2.99. Mp: 237−240 °C.

$\{2\text{-}[(\mathrm{CH_3})_2\mathrm{NCH_2}]_2\mathrm{C_6H_4}\}_2\mathrm{Sn}(\mathrm{OCH_2CH_2O})$ (2e). An excess of ethylene glycol (5 mL, 71.6 mmol) and **2** (1 g, 1.25 mmol) were refluxed in benzene (30 mL) in a Dean−Stark apparatus for 3 h, giving a white solid after vacuum evaporation. The solid was washed with hexane and crystallized from diethyl ether in 74% yield. ^{1}H NMR (500.13 MHz, C_6D_6, 300 K, ppm): 7.95 (broad, 2H, H(6), $^3J(^1\mathrm{H},^{119}\mathrm{Sn}) = 86$ Hz); 7.28 (broad, 4H, H(4,5)); 7.10 (broad, 2H, H(3)); 3.63 (broad, 4H, OCH_2); 3.46 (s, 4H, NCH_2); 2.06 (s, 12H, $N(CH_3)_2$). ^{119}Sn{^{1}H} NMR (C_6D_6, 300 K, ppm): −243.6. Anal. Found: C, 53.6; H, 6.2; N, 6.2. Calcd for $C_{20}H_{28}N_2O_2Sn$ (447.15): C, 53.72; H, 6.31; N, 6.26. Mp: 230−232 °C. Single crystals of **2e**·$^1/_2HOCH_2CH_2OH$ were obtained by crystallization of the crude product from ethylene glycol.

Catalytic Tests. The tests were performed in stainless steel autoclaves with a separated loop to allow easy handling of the catalyst under argon and its reaction with a definite epoxide/CO_2 mixture (ca. 80 °C and 80 bar CO_2) similar to the procedure reported in detail in earlier contributions.[21] IR and ^{1}H and ^{13}C NMR spectroscopy was used to assess the nature of the carbonate (cyclic monomer or polymer) and evaluate the efficiency of the CO_2 insertion. The tests were carried out using a 1:1000 catalyst to substrate molar ratio and a large excess of carbon dioxide (a ca. 2- to 3-fold excess relative to the epoxide), in agreement with standard procedures reported in the relevant CO_2 literature.[22]

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Supporting Information Available: Text, figures, tables, and CIF files giving the molecular structure of **2e**·$HOCH_2CH_2OH$, calculated energetic parameters, an IR spectrum of the catalytic test product, a hypothetical mechanism of CO_2 activation, and crystallographic parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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